COMPARISON OF INORGANICS IN THREE LOW-RANK COALS

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INTRODUCTION

In the use of low-rank coals it has been found that inorganic materials present in these coals can have adverse effects on process performance. During combustion processes some inorganics are liberated and react with other inorganics causing combustor fouling problems (1). The unique characteristics of the flyash produced upon combustion, frequently, if concentrations of sodium and sulfur are low, produces a high resisitivity ash making it difficult to collect in an electrostatic precipitator (2). In fluidized bed combustion, the inorganics of some low-rank coals can be used for sulfur retention (3) but bed agglomeration is a problem with high concentrations of sodium (4). In coal conversion processes the inorganic material can serve either as catalysts or catalyst poisons.

The occurrence of inorganic materials in low-rank coals is very complex. They are present as discrete mineral phases, as ions held by ion pair bonding with carboxyl groups or clays, and as coordinated metal ions. Knowledge of the distribution of inorganics within the coal could be used to predict effects in a given process.

We have chosen to compare the way in which inorganic material is found in three coals. These coals are two lignites from the Beulah mine, North Dakota, and the Bryan Mine, Texas and one subbituminous coal from the Rosebud mine, Montana.

EXPERIMENTAL

The coals were treated using a method modified from the procedure reported by Miller and Given (5). Figure 1 shows a flow sheet of the procedure used to examine the various coals. Each coal was ground to approximately 400 mesh in an alumina grinding apparatus. The ground coal was dried using a freeze drier. Analysis of the dried coal was performed using x-ray fluorescence (XRF) and neutron activation analysis (NAA). Duplicate samples were run by placing 15-20 g of coal in a plastic beaker with 100 ml of 1M ammonium acetate. This was heated to about 70°C and stirred for 20 hours. The sample was filtered, the residue washed and dried. The solution was transferred to a 500 ml volumetric flask and made up to volume.

The solution was analyzed by inductively coupled argon plasma spectroscopy (ICAP). Samples of the residue were analyzed by XRF and NAA. The residue was treated a second time with ammonium acetate followed by two 1M hydrochloric acid extractions using the same procedure as ammonium acetate extraction.

XRF analyses were performed using the energy-dispersive Kevex* 0700 subsystem. ICAP analysis were obtained using a Jarrell-Ash Mark I Model 975* multi-element analyzer. Analysis is controlled by a computer using a program for 22 elements. Neutron activation analysis used in this study was performed at North Carolina State University. The system and procedures have been described elsewhere (6).

RESULTS:

The table following shows the initial analysis of the three coals under consideration.

TABLE I

INITIAL ANALYSIS OF COALS, PARTS PER MILLION

Analysis	Beulah N.D. Lignite	Bryan Texas Lignite	Rosebud Montana Sub-bituminous
Al	3940	12360	3370
Ba	630	190	190
Ca	12800	7130	3520
Cr	3	21	4
Cu	22	24	30
Fe	5000	20950	8450
K	930	1970	120
Mg	2490	2000	920
Mn	58	300	35
Na	4340	310	87
Ni	22	40	52
Sr	485	80	90
Ti	185	1410	280
Ash	9.5%	24.5%	4.9%

These are followed by the anaylses obtained after the samples had been extracted twice with ammonium acetate. Table II shows the amount extracted from the original coal and the percent of the original.

Table III contains the results of the samples which have been extracted twice by hydrochloric acid. The amount extracted and the percent of the original coal are given.

DISCUSSION

Examination of the initial analysis reveals the dramatic differences in the amounts of inorganic material between the three coals. Aluminum, iron, potassium, and titanium are very high in the Bryan coal compared to the values for the Beulah and Rosebud coals. In general, the Bryan has a much high inorganic content which

*Reference to specific brand names does not imply endorsement by the U.S. Department of Energy.

TABLE II

ANALYSIS OF COALS AFTER EXTRACTION WITH AMMONIUM ACETATE

Analysis	Beulah PPM Extracted	Beulah % Extracted	Bryan PPM Extracted	Bryan % Extracted	Rosebud PPM Extracted	Rosebud % Extracted
Al						< 1
Ba	239	38	53	28	57	30
Ca	9728	76	442	62	2003	56
Cr			3	14		
Cu						
Fe						< 1
K	186	20	177	9	2	2
Mg	2241	90	1880	94	598	65
Mn	17	30	129	43	7	20
Na	3645	84	232	75	70	81
Ni						
Sr	422	87	65	81	22	90
Ti						
Ash remaining		4.9		23.8		3.8

TABLE III

ANALYSIS OF COALS AFTER EXTRACTION WITH HYDROCHLORIC ACID

Analysis	Beulah PPM Extracted	Beulah % Extracted	Bryan PPM Extracted	Bryan % Extracted	Rosebud PPM Extracted	Rosebud % Extracted
Al	2750	70	2719	22	1213	36
Ba	378	60	104	55	116	61
Ca	2688	21	1283	18	1408	40
Cr	1.5	51	9	41	1.5	37
Cu	21	90	10	76	5	18
Fe	1950	39	14246	68	5154	61
K			157	8	24	20
Mg	100	4	120	6	257	28
Mn	40	70	153	51	24	70
Na	43	1	9	3	10	12
Ni	6	27	21	52	3	5
Sr	63	13	15	19	56	63
Ti	22	12	409	29	154	55
Ash remaining		1.2		22.6		2.8

can also be seen by referring to the ash content listed in Table I. Further note should be taken of the high sodium content for the Beulah coal and related combustion problems (1).

The ammonium acetate extraction removes those inorganics associated as ions held by ion pair bonds to the carboxyl groups or to the clay minerals. The result of this extraction procedure is summarized in Table 2. For Beulah lignite most of the Ca, Na, Mg and Sr are bound to the carboxyl groups or possibly with the clays. The Bryan and Rosebud coals show similar trends for Ca, Na, and Sr. On the other hand, the Mg in Rosebud indicates a different association in the coal.

The hydrochloric acid extractions remove those species present in the coals as oxides, carbonate minerals, and coordinated metal ions. Larger discrepancies were noted between the coals extracted with HCl than ammonium acetate extracted. The fact that 70% of the Al is removed from Beulah is possibly explained by it being removed from the clay materials (7) but this is not well understood. Of particular interest is the removal of Ca, Mg and Sr in the Rosebud, which suggest that these elements were present as carbonate minerals. This relationship has also been suggested by Finkelman (8). The Fe is present in the coals as possibly a carbonate (siderite), oxide, and pyrite.

The changes in percent ash determined in the coal, after the ammonium acetate and HCl extractions reveal large changes in the amount of ash in Beulah and Rosebud. The total amount of inorganics removed by the ammonium acetate of the Beulah is approximately 48%. The percentage of ash removed for Rosebud was approximately 22% with ammonium acetate. The Bryan lignite has only 3% of its ash associated with the ion exchangeable fraction. The major inorganic constituents remaining in the coals after both extractions consist of quartz, clays and pyrite.

CONCLUSIONS

The alkaline and alkaline earth metals in all three coals are partially or totally removed with ammonium acetate extraction. The major differences between the coals are:

1. 48% of the total inorganics of the Beulah are removed with ammonium acetate by far the highest of 3 coals.

2. Bryan Texas lignite consists of mostly extraneous mineral matter including clays and quartz minerals (9).

3. The Rosebud subbituminous has higher percentages of Mg, Ca, and Sr associated as carbonates, revealed in the HCl extractions.

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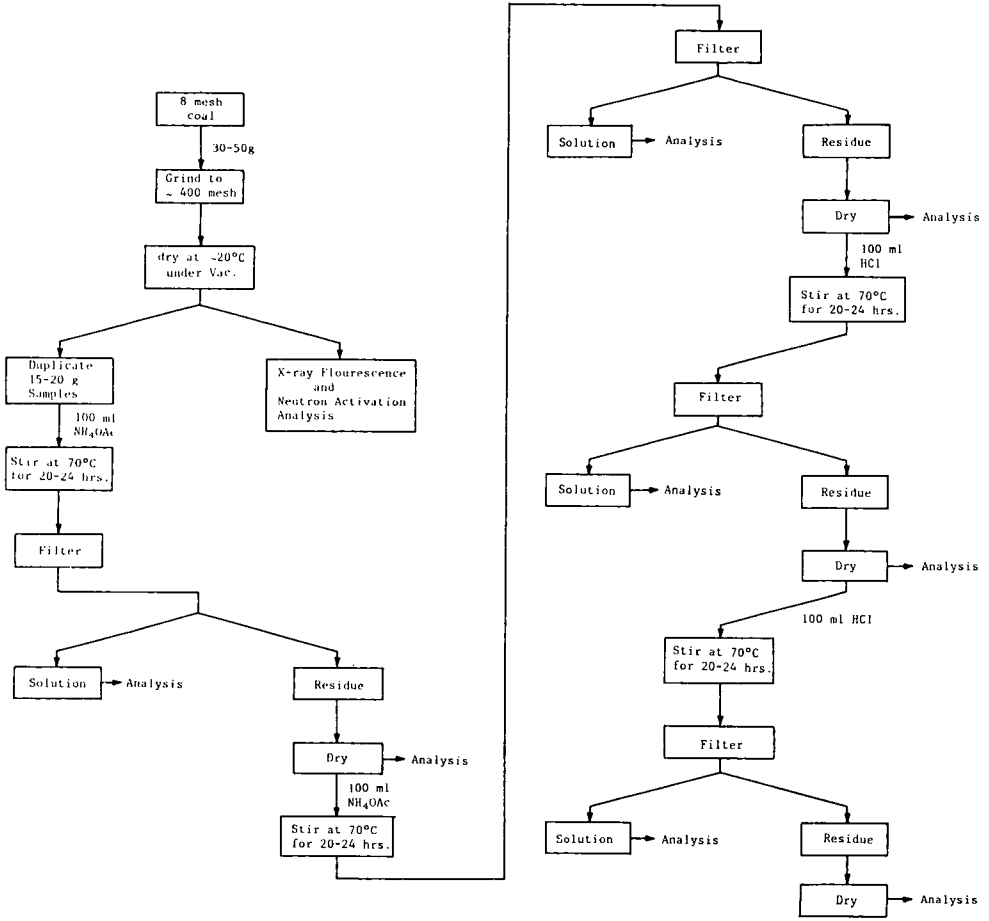

FIGURE 1. Flow diagram of extraction procedure.